

# Work Relation and the Second Law of Thermodynamics in Nonequilibrium Steady States

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We extend Jarzynski's work relation and the second law of thermodynamics to a heat conducting system which is operated by an external agent. These extensions contain a new nonequilibrium contribution expressed as the violation of the (linear) response relation caused by the operation. We find that a natural extension of the minimum work principle involves information about the time-reversed operation, and is far from straightforward. Our work relation may be tested experimentally especially when the temperature gradient is small.

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Thermodynamics is a universal framework for macroscopic systems in equilibrium. The second law, which is at the heart of thermodynamics, gives strict limitations to macroscopic operations and provides fundamental concepts such as irreversibility and minimum work. The idea of minimum work leads to the useful Gibbs relation, which represents work associated with a thermodynamic operation as the difference in the free energy. To develop similar useful thermodynamics for nonequilibrium systems is a fascinating challenge. In [1–7], attempt has been made to construct operational thermodynamics for nonequilibrium steady states (NESS). A central idea was to replace the “bare heat” in NESS by its “renormalized” counterpart called excess heat.

Recently there has been a considerable progress in nonequilibrium physics which in particular led to the fluctuation theorem [8] and the Jarzynski equality [9, 10]. The former gives an exact equality for the entropy production in NESS, which is connected to response relations. The latter provides an exact relation between operational work and the free energy not only in quasi-static but also in general operations in equilibrium. It is also directly connected to the second law of thermodynamics.

In the present Letter, we focus on mechanical work associated with an external operation in NESS realized in classical heat conducting systems. We derive a very natural extension (1) of the Jarzynski equality to NESS, which may be tested experimentally. The extended equality straightforwardly implies the Gibbs relation (3) for the quasi-static limit and the second law (4). These relations contain new nonequilibrium contributions expressed as the violation caused by the external operation of the linear response relation. The derivation of the results are essentially straightforward and is based on the detailed fluctuation theorem (also known as the microscopic reversibility or the local detailed balance condition). We hope that these findings become crucial steps in the understanding and construction of thermodynamics for NESS.

*Setup:* Our theory can be developed in various nonequilibrium settings of classical stochastic systems. For simplicity we here focus on heat conduction, and consider a system which is attached to two heat baths with inverse temperatures  $\beta_1$  and  $\beta_2$  and has controllable parameters  $\nu$ . An example is a system of  $N$  particles in a container in which the position  $\nu$  of one of the particles is controlled by the external agent (see Fig. 1). The inverse temperatures  $\beta_1$  and  $\beta_2$  are fixed throughout, and are often omitted. We define  $\bar{\beta} := (\beta_1 + \beta_2)/2$  and  $\Delta\beta := \beta_1 - \beta_2$ .

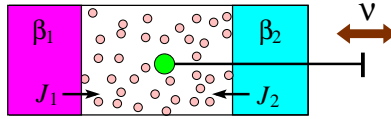


FIG. 1: An example of the system, where the position  $\nu$  of a particle (green online) can be controlled externally.  $J_1$  and  $J_2$  are the heat currents from the heat baths to the system.

The coordinates of  $N$  particles are collectively denoted as  $\Gamma = (\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{p}_1, \dots, \mathbf{p}_N)$ , and its time-reversal as  $\Gamma^* = (\mathbf{r}_1, \dots, \mathbf{r}_N; -\mathbf{p}_1, \dots, -\mathbf{p}_N)$ . The time evolution of the system is governed by deterministic dynamics according to the Hamiltonian  $H_\nu(\Gamma)$  and stochastic Markovian dynamics due to coupling to the two external heat baths. We impose time-reversal symmetry  $H_\nu(\Gamma) = H_\nu(\Gamma^*)$ . When discussing time evolution of  $\Gamma$ , we denote by  $\Gamma(t)$  its value at time  $t$ , and by  $\hat{\Gamma} = (\Gamma(t))_{t \in [-\tau_\ell, \tau_\ell]}$  the path in the whole time interval  $[-\tau_\ell, \tau_\ell]$ . The heat baths may be realized in standard manners such as “thermal walls” (see, e.g. [11]) or the Langevin noise near the walls. The only (and the essential) requirement is that the detailed fluctuation theorem (see (11) below) is valid. By  $J_k(\hat{\Gamma}; t)$ , we denote the

heat current that flows from the  $k$ -th bath to the system at time  $t$  in the path  $\hat{\Gamma} = (\Gamma(t))_{t \in [-\tau_\ell, \tau_\ell]}$  [12]. We write  $J(\hat{\Gamma}; t) = (J_1(\hat{\Gamma}; t) - J_2(\hat{\Gamma}; t))/2$ , which is the heat current from the first to the second heat bath.

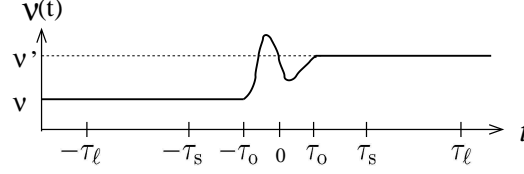


FIG. 2: A sketch of the protocol  $\hat{\nu}$ . We assume  $\tau_\ell - \tau_s \gg \tau_r$  and  $\tau_s - \tau_o \gg \tau_r$  where  $\tau_r$  is the relaxation time of the system.

We shall assume that the system settles to a unique NESS when it evolves for a sufficiently long time with fixed  $\nu$ . For later convenience we shall choose and fix three time scales  $0 < \tau_o < \tau_s < \tau_\ell$  such that  $\tau_\ell - \tau_s \gg \tau_r$  and  $\tau_s - \tau_o \gg \tau_r$  where  $\tau_r$  is the relaxation time of the system. See Fig. 2. We suppose that an external agent performs an operation to the system by changing the parameters  $\nu$  according to a prefixed protocol. A protocol is specified by a function  $\nu(t)$  of  $t \in [-\tau_\ell, \tau_\ell]$ . In order to study transitions between NESS, we assume that  $\nu(t)$  varies only for  $t \in [-\tau_o, \tau_o]$ , so that  $\nu(t) = \nu$  for  $t \in [-\tau_\ell, -\tau_o]$  and  $\nu(t) = \nu'$  for  $t \in [\tau_o, \tau_\ell]$ . We denote by  $\hat{\nu} = (\nu(t))_{t \in [-\tau_\ell, \tau_\ell]}$  the whole protocol, by  $\hat{\nu}^\dagger = (\nu(-t))_{t \in [-\tau_\ell, \tau_\ell]}$  the time-reversal of  $\hat{\nu}$ , and by  $(\nu)$  the protocol in which the parameters are kept constant at  $\nu$ . During the operation, the external agent performs mechanical work  $W(\hat{\Gamma}) = \int_{-\tau_o}^{\tau_o} dt \partial_\nu H_\nu(\Gamma(t))|_{\nu=\nu(t)} \dot{\nu}(t)$  to the system. We denote by  $Q_t(\hat{\Gamma}) = \int_{-\tau_s}^{\tau_s} dt J(\hat{\Gamma}; t)$  the heat transferred from the first to the second heat bath during  $[-\tau_s, \tau_s]$ . Similarly, we write  $Q_t^i(\hat{\Gamma}) = \int_{-\tau_\ell}^{-\tau_s} dt J(\hat{\Gamma}; t)$  and  $Q_t^f(\hat{\Gamma}) = \int_{\tau_s}^{\tau_\ell} dt J(\hat{\Gamma}; t)$ .

The time evolution of the system is described by a Markov process. We denote by  $\mathcal{T}_\nu[\hat{\Gamma}]$  the transition probability associated with a path  $\hat{\Gamma}$  in a protocol  $\hat{\nu}$ . It is normalized as  $\int \mathcal{D}\hat{\Gamma} \mathcal{T}_\nu[\hat{\Gamma}] \delta(\Gamma(-\tau_\ell) - \Gamma_i) = 1$  for any initial state  $\Gamma_i$ , where  $\int \mathcal{D}\hat{\Gamma}(\dots)$  denotes the integral over all the possible paths  $\hat{\Gamma}$ . For any function  $f(\hat{\Gamma})$ , we define its average in the protocol  $\hat{\nu}$  as  $\langle f \rangle^{\hat{\nu}} := \int \mathcal{D}\hat{\Gamma} \rho_\nu^{\text{st}}(\Gamma(-\tau_\ell)) \mathcal{T}_\nu[\hat{\Gamma}] f(\hat{\Gamma})$ , where  $\rho_\nu^{\text{st}}(\Gamma)$  is the probability distribution for the unique NESS corresponding to the parameters  $\nu = \nu(-\tau_\ell)$ .

*Jarzynski equality for NESS:* In [15], we introduced a nonequilibrium free energy  $F(\nu)$  which is a function of the parameter  $\nu$  (as well as  $\beta_1$  and  $\beta_2$ ), and coincides with the equilibrium free energy for  $\beta_1 = \beta_2$ . Here we show that, for any  $\beta_1, \beta_2$ , and operation  $\hat{\nu}$ , the exact identity

$$\langle e^{-\bar{\beta}(W - \Delta F)} \rangle^{\hat{\nu}} = \langle e^{\Delta\beta Q_t} \rangle_{\text{m}}^{\hat{\nu}^\dagger}, \quad (1)$$

is valid, where  $\Delta F := F(\nu') - F(\nu)$ . The identity (1) is our most basic result. Here we introduced a modified expectation

$$\langle f \rangle_{\text{m}}^{\hat{\nu}} := \frac{\langle e^{\Delta\beta Q_t^i/2} f e^{\Delta\beta Q_t^f/2} \rangle^{\hat{\nu}}}{\langle e^{\Delta\beta Q_t^i/2} e^{\Delta\beta Q_t^f/2} \rangle^{\hat{\nu}}}, \quad (2)$$

where  $f(\hat{\Gamma})$  is an arbitrary function [13]. Obviously (1) reduces to the celebrated Jarzynski equality for  $\beta_1 = \beta_2$ . We would like to propose (1) as the most natural nonequilibrium extension of the Jarzynski equality to NESS.

Let us stress that  $W(\hat{\Gamma})$  is the standard mechanical work, and the left-hand side of (1) can be evaluated experimentally (exactly as in the case of the original Jarzynski equality). Although the right-hand side may appear artificial, we shall show below that this quantity can also be evaluated experimentally (at least when the NESS is close to equilibrium). To be specific, we show below in (7) that this modified expectation is directly connected to the well-known linear response relation by rewriting the modified expectation in terms of heat currents. We recall that  $\langle \dots \rangle^{\hat{\nu}^\dagger}$  represents the average in a physically natural time evolution with the time-reversed protocol.

We also note that since  $W(\hat{\Gamma}) = 0$  for a constant protocol  $\hat{\nu} = (\nu)$ , the equality (1) implies  $\langle e^{\Delta\beta Q_t} \rangle_{\text{m}}^{(\nu)} = 1$ . This is a version of the integrated fluctuation theorem and is related to a response relation as usual (see [14]). We can say that the equality (1) reveals an intimate relation between the mechanical work in NESS and the response relation. We shall see later that a deviation of  $\langle e^{\Delta\beta Q_t} \rangle_{\text{m}}^{\hat{\nu}}$  from 1 corresponds to a violation of the response relation.

*Quasi-static limit:* Since  $W(\hat{\Gamma})$  essentially does not fluctuate in the quasi-static limit, one has  $\langle e^{-\bar{\beta}W} \rangle^{\hat{\nu}} = e^{-\bar{\beta}\langle W \rangle^{\hat{\nu}}}$ . By also noting that  $\langle W \rangle^{\hat{\nu}^\dagger} = -\langle W \rangle^{\hat{\nu}}$  in this limit, (1) reduces to

$$\langle W \rangle^{\hat{\nu}} = \Delta F + \bar{\beta}^{-1} \log \langle e^{\Delta\beta Q_t} \rangle_{\text{m}}^{\hat{\nu}}, \quad (3)$$

which is an exact relation corresponding to the Gibbs relation in equilibrium thermodynamics.

The equilibrium Gibbs relation leads to potentials which describe macro- or mesoscopic forces. The equality (3), however, implies that we may not have such potentials in NESS as  $\log\langle e^{\Delta\beta Q_t} \rangle_m^{\hat{\nu}}$  is not necessarily described by a difference of a state function.

*The second law for NESS:* From Jensen's inequality, we have  $\log\langle e^{-\bar{\beta}(W-\Delta F)} \rangle^{\hat{\nu}} \geq -\bar{\beta}(\langle W \rangle^{\hat{\nu}} - \Delta F)$ , which implies

$$\langle W \rangle^{\hat{\nu}} \geq \Delta F - \bar{\beta}^{-1} \log\langle e^{\Delta\beta Q_t} \rangle_m^{\hat{\nu}^\dagger}, \quad (4)$$

where the equality holds in the quasi-static limit. We believe that this is a natural extension of the second law of thermodynamics to operations between NESS. It is notable that the right-hand side involves a quantity in the reversed protocol  $\hat{\nu}^\dagger$ .

The inequality (4) implies that the minimum work principle is not extended straightforwardly to NESS. The quantity equated with the free energy difference is not the work but the sum of the work and  $\bar{\beta}^{-1} \log\langle e^{\Delta\beta Q_t} \rangle_m^{\hat{\nu}^\dagger}$ . This apparently means that one must invoke the reversed protocol  $\hat{\nu}^\dagger$  to find the limitation of the work.

*Expansion in weak nonequilibrium regime:* We define a dimensionless parameter indicating the degree of nonequilibrium by  $\epsilon = |\Delta\beta|/\bar{\beta}$ . We here deal with systems with small  $\epsilon$  and ignore the contribution of  $O(\epsilon^3)$ .

Let us now derive a compact approximate expression (7) for the right-hand side of (1). From the definition (2) of the modified expectation, we have

$$\log\langle e^{\Delta\beta Q_t} \rangle_m^{\hat{\nu}} = \log\langle e^{\Delta\beta Q_t^i/2} e^{\Delta\beta Q_t} e^{\Delta\beta Q_t^f/2} \rangle^{\hat{\nu}} - \log\langle e^{\Delta\beta Q_t^i/2} e^{\Delta\beta Q_t^f/2} \rangle^{\hat{\nu}}. \quad (5)$$

By applying the cumulant expansion to the right-hand side and arranging the result by order, we have

$$\log\langle e^{\Delta\beta Q_t} \rangle_m^{\hat{\nu}} = \Delta\beta\langle Q_t \rangle^{\hat{\nu}} + \frac{\Delta\beta^2}{2}\langle Q_t; (Q_t^i + Q_t + Q_t^f) \rangle^{\hat{\nu}} + O(\epsilon^3), \quad (6)$$

where  $\langle A; B \rangle = \langle AB \rangle - \langle A \rangle \langle B \rangle$ . Since  $Q_t(\hat{\Gamma}) = \int_{-\tau_s}^{\tau_s} dt J(\hat{\Gamma}; t)$  and  $Q_t^i(\hat{\Gamma}) + Q_t(\hat{\Gamma}) + Q_t^f(\hat{\Gamma}) = \int_{-\tau_\ell}^{\tau_\ell} dt J(\hat{\Gamma}; t)$ , we have

$$\log\langle e^{\Delta\beta Q_t} \rangle_m^{\hat{\nu}} = \Delta\beta \int_{-\tau_s}^{\tau_s} dt J_{\text{viol}}^{\hat{\nu}}(t) + O(\epsilon^3), \quad (7)$$

where we have defined

$$J_{\text{viol}}^{\hat{\nu}}(t) = \langle J(t) \rangle^{\hat{\nu}} + \frac{\Delta\beta}{2} \int_{-\tau_\ell}^{\tau_\ell} ds \langle J(t); J(s) \rangle^{\hat{\nu}}. \quad (8)$$

In the steady protocol ( $\nu$ ), we have the linear response relation (LRR) for heat currents [17, 18] and thus  $J_{\text{viol}}^{(\nu)}(t) = 0$  (more exactly,  $O(\epsilon^2)$ ). More generally the equality  $\langle e^{\Delta\beta Q_t} \rangle_m^{(\nu)} = 1$  gives an exact response relation for  $\langle J(t) \rangle^{(\alpha)}$  because it connects  $\langle J(t) \rangle^{(\alpha)}$  to the higher cumulants of  $J(\hat{\Gamma}; t)$ .

When there is an operation, the LRR is violated in general and  $J_{\text{viol}}^{\hat{\nu}}(t)$  does not vanish. We can thus interpret  $J_{\text{viol}}^{\hat{\nu}}(t)$  as the “violation of LRR” due to the external operation. Similarly, the deviation of  $\langle e^{\Delta\beta Q_t} \rangle_m^{\hat{\nu}}$  from 1 can be regarded as the violation of the exact response relation. We have thus reached the most important interpretation of the equality (1); the mechanical work in NESS is related to the violation of the response relation.

In equilibrium operations at  $\Delta\beta = 0$ , we see that  $J_{\text{viol}}^{\hat{\nu}}(t) = \langle J(t) \rangle^{\hat{\nu}}$  corresponds to the heat current induced by the external operation. This enables us to intuitively understand the role played by  $J_{\text{viol}}^{\hat{\nu}}(t)$  in a weak NESS. In an equilibrium system the induced current  $\langle J(t) \rangle^{\hat{\nu}}$  requires no “costs”, and hence does not appear in thermodynamic relations. In a NESS, on the other hand, any heat current is coupled to the temperature difference. This is the reason that we have  $\Delta\beta\langle J(t) \rangle^{\hat{\nu}}$  in our thermodynamic relation.

*Derivation of (17):* We shall prove our main observation (1). The proof relies on the detailed fluctuation theorem (11) and the exact representation (14) for the probability distribution of NESS. It is essentially straightforward.

Let us decompose the time intervals as  $[-\tau_\ell, \tau_\ell] = [-\tau_\ell, -\tau_s] \cup [-\tau_s, \tau_s] \cup [\tau_s, \tau_\ell]$ , and, correspondingly, a path as  $\hat{\Gamma} = (\hat{\Gamma}_i, \hat{\Gamma}_m, \hat{\Gamma}_f)$ . For an arbitrary function  $f$  of  $\hat{\Gamma}_m = (\Gamma(t))_{t \in [-\tau_s, \tau_s]}$ , the following expectation is naturally decomposed as

$$\langle e^{\Delta\beta Q_t^i(\hat{\Gamma})/2} f e^{\Delta\beta Q_t^f(\hat{\Gamma})/2} \rangle^{\hat{\nu}} = \int d\Gamma d\Xi \langle e^{\Delta\beta Q_t^i(\hat{\Gamma})/2} \rangle_{\text{st}, \Gamma}^{(\nu)} [f]_{\Gamma, \Xi}^{\hat{\nu}} \langle e^{\Delta\beta Q_t^f(\hat{\Gamma})/2} \rangle_{\Xi, \text{st}}^{(\nu)}, \quad (9)$$

where we used  $Q_t^i(\hat{\Gamma}) = Q_t^i(\hat{\Gamma}_i)$  and  $Q_t^f(\hat{\Gamma}) = Q_t^f(\hat{\Gamma}_f)$ .  $\langle \cdots \rangle_{\text{st}, \Gamma}$  or  $\langle \cdots \rangle_{\Xi, \text{st}}$  is properly defined conditioned expectation with a fixed final state  $\Gamma$  or initial state  $\Xi$  [16]. We also introduced unnormalized expectation  $[\cdots]$  by

$$[f]_{\Gamma, \Xi}^{\hat{\nu}} = \rho_{\nu}^{\text{st}}(\Gamma) \int \mathcal{D}\hat{\Gamma}_m f(\hat{\Gamma}_m) \delta(\Gamma(-\tau_s) - \Gamma) \delta(\Gamma(\tau_s) - \Xi) \mathcal{T}_{\hat{\nu}}[\hat{\Gamma}_m], \quad (10)$$

where  $\mathcal{T}_{\hat{\nu}}[\hat{\Gamma}_m]$  is the transition probability for  $\hat{\Gamma}_m$ .

The transition probability  $\mathcal{T}_{\hat{\nu}}[\hat{\Gamma}_m]$  is known to satisfy the detailed fluctuation theorem,

$$\mathcal{T}_{\hat{\nu}}[\hat{\Gamma}_m] e^{\sum_{k=1}^2 \beta_k Q_k(\hat{\Gamma}_m)} = \mathcal{T}_{\hat{\nu}^\dagger}[\hat{\Gamma}_m^\dagger], \quad (11)$$

where  $\mathcal{T}_{\hat{\nu}^\dagger}[\hat{\Gamma}_m^\dagger]$  is the transition probability of the time reversed path  $\hat{\Gamma}_m^\dagger = (\Gamma(-t))_{t \in [-\tau_s, \tau_s]}$  for the reversed protocol  $\hat{\nu}^\dagger$ .  $Q_k(\hat{\Gamma}_m) = \int_{-\tau_s}^{\tau_s} dt J_k(\hat{\Gamma}_m; t)$  is the total heat that flows from the bath  $k$  to the system during the path  $\hat{\Gamma}_m$ . By using the energy conservation  $H_{\nu'}(\Gamma(\tau_s)) - H_{\nu}(\Gamma(-\tau_s)) = W(\hat{\Gamma}_m) + \sum_{k=1}^2 Q_k(\hat{\Gamma}_m)$ , (11) is rewritten as

$$e^{-\bar{\beta} H_{\nu}(\Gamma(-\tau_s)) - \bar{\beta} W(\hat{\Gamma}_m)} \mathcal{T}_{\hat{\nu}}[\hat{\Gamma}_m] = e^{-\bar{\beta} H_{\nu'}(\Gamma(\tau_s)) + \Delta\beta Q_t(\hat{\Gamma}_m^\dagger)} \mathcal{T}_{\hat{\nu}^\dagger}[\hat{\Gamma}_m^\dagger], \quad (12)$$

where we noted that  $Q_t(\hat{\Gamma}_m^\dagger) = -Q_t(\hat{\Gamma}_m)$ . By integrating over  $\hat{\Gamma}_m$  with constraints  $\Gamma(-\tau_s) = \Gamma$  and  $\Gamma(\tau_s) = \Xi$ , and recalling (10), we have

$$\frac{e^{-\bar{\beta} H_{\nu}(\Gamma)}}{\rho_{\nu}^{\text{st}}(\Gamma)} [e^{-\bar{\beta} W}]_{\Gamma, \Xi}^{\hat{\nu}} = \frac{e^{-\bar{\beta} H_{\nu'}(\Xi)}}{\rho_{\nu'}^{\text{st}}(\Xi)} [e^{\Delta\beta Q_t}]_{\Xi^*, \Gamma^*}^{\hat{\nu}^\dagger}. \quad (13)$$

In [15], we derived (also by using the detailed fluctuation theorem (11)) the exact representation for the probability distribution in NESS with parameters  $\nu$ ,

$$\rho_{\nu}^{\text{st}}(\Gamma) = e^{\bar{\beta}(F(\nu) - H_{\nu}(\Gamma))} \frac{\langle e^{\Delta\beta Q_t^f/2} \rangle_{\Gamma^*, \text{st}}^{(\nu)}}{\langle e^{\Delta\beta Q_t^i/2} \rangle_{\text{st}, \Gamma}^{(\nu)}}, \quad (14)$$

where the normalization factor  $F(\nu)$  was identified as a nonequilibrium free energy. By substituting (14) into (13), one gets

$$e^{\bar{\beta} F(\nu)} \langle e^{\Delta\beta Q_t^i/2} \rangle_{\text{st}, \Gamma}^{(\nu)} [e^{-\bar{\beta} W}]_{\Gamma, \Xi}^{\hat{\nu}} \langle e^{\Delta\beta Q_t^f/2} \rangle_{\Xi, \text{st}}^{(\nu')} = e^{\bar{\beta} F(\nu')} \langle e^{\Delta\beta Q_t^i/2} \rangle_{\text{st}, \Xi^*}^{(\nu')} [e^{\Delta\beta Q_t}]_{\Xi^*, \Gamma^*}^{\hat{\nu}^\dagger} \langle e^{\Delta\beta Q_t^f/2} \rangle_{\Gamma^*, \text{st}}^{(\nu)} \quad (15)$$

By integrating over  $\Gamma$  and  $\Xi$ , and using (10), this implies

$$\langle e^{\Delta\beta Q_t^i/2} e^{-\bar{\beta}(W - \Delta F)} e^{\Delta\beta Q_t^f/2} \rangle^{\hat{\nu}} = \langle e^{\Delta\beta Q_t^i/2} e^{\Delta\beta Q_t} e^{\Delta\beta Q_t^f/2} \rangle^{\hat{\nu}^\dagger}. \quad (16)$$

Noting that  $\langle e^{\Delta\beta Q_t^i/2} e^{\Delta\beta Q_t^f/2} \rangle^{\hat{\nu}} = \langle e^{\Delta\beta Q_t^i/2} e^{\Delta\beta Q_t^f/2} \rangle^{\hat{\nu}^\dagger}$  [19], this reduces to

$$\langle e^{-\bar{\beta}(W - \Delta F)} \rangle_m^{\hat{\nu}} = \langle e^{\Delta\beta Q_t} \rangle_m^{\hat{\nu}^\dagger}. \quad (17)$$

Since the operation takes place in the interval  $[-\tau_o, \tau_o]$ , there is no correlation between  $W(\hat{\Gamma})$  and  $e^{\Delta\beta Q_t^i/2}$  or  $e^{\Delta\beta Q_t^f/2}$ . This means that the left-hand side of (17) can be replaced by the usual expectation to give the desired (1).

*Discussions:* We have derived nonequilibrium extensions of the Jarzynski work relation (1), the Gibbs relation (3), and the second law (4) in a general classical model of heat conduction. Although one can show that the Gibbs relation (3) approximated to  $O(\epsilon^2)$  coincides with the extended Clausius relation that we have derived in [7], all the other results are novel. Especially, it is fascinating that thermodynamic relations and response relations are coupled intrinsically in our relations. The traditional understanding has been that thermodynamic relations work for equilibrium operations, and response relations work for nonequilibrium steady states. Here, by considering an operation for NESS and proving the extended Jarzynski equality (1), we have shown that the two paradigms are naturally unified in a single exact relation.

There has been many works on the violation of fluctuation-dissipation relation including an effective temperature for characterizing relaxation processes [20], the formula for estimating the energy dissipation [21, 22], and the linear response around NESS [23, 24]. It would be suggestive to look for possible relations of these topics with the present study.

Although we have restricted ourselves to the simplest setting here, it is straightforward to extend the present results to the case where the inverse temperatures  $\beta_1$  and  $\beta_2$  vary, or to other nonequilibrium systems. The only essential requirement is the detailed fluctuation theorem (11).

Last but not least let us stress that all of our main results (1), (3), and (4) may be tested experimentally especially when the degree of nonequilibrium  $\epsilon$  is small. Although we still do not know whether these results have practical applications, it would be exciting to imagine applying the exact Jarzynski equality (1) to the analysis of the efficiency of a thermodynamic machine operating in NESS.

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